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AFRPL-TR-66-272

(Unclassified title)

**KINETICS OF DECOMPOSITION  
OF SOLID OXIDIZERS**

**QUARTERLY TECHNICAL REPORT AFRPL - TR - 66 - 272**

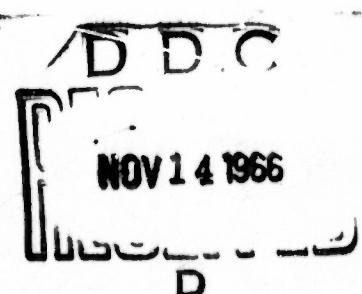
**(1 July 1966 to 30 September 1966)**

**15 October 1966**

**AIR FORCE ROCKET PROPULSION LABORATORY  
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**THE DOW CHEMICAL COMPANY**

MIDLAND, MICHIGAN 48640

October 15, 1966

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QUARTERLY TECHNICAL REPORT NO. 3 (U)  
(1 July - 30 September 1966)

KINETICS OF DECOMPOSITION  
OF SOLID OXIDIZERS (U)

October 15, 1966

Dow Report NF-3Q-66

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## FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, on Air Force Contract Nr. AF 04(611)-11395, BPSN 623148, Project Number 3148, "Kinetics of Decomposition of Solid Oxidizers." This work was sponsored and administered by Air Force Rocket Propulsion Laboratory, Research and Technology Division, Edwards, California, Air Force Systems Command, United States Air Force, with Dr. William J. Leahy as project officer.

The report represents the work performed on this contract for the period of 1 July 1966 and 30 September 1966, and is being submitted as Quarterly Progress Report No. 3 as part of the contract commitment.

Management direction at Dow is under Dr. R. P. Ruh, Laboratory Director of the Scientific Projects Laboratory, and supervised by Dr. D. A. Rausch, Division Leader. Dr. J. P. Flynn and Mr. T. E. Dergazarian are the principal investigators. Dr. R. G. Pearson, Northwestern University, is a consultant to the project.

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## SECTION I

### ABSTRACT (U)

(U) The purpose of this research has been to study the thermal decomposition of the solid oxidizers, INFO-635P, poly FA-BDE, and BTU. The objective is to obtain knowledge of their decomposition kinetics and mechanism and their relationship to the high sensitivity of these materials.

(C) Thermal decompositions of poly FA-BDE in the monel system were continued with additional experiments in the temperature range 160°-180°C. This work was done both at low pressure of decomposition gases and under continuous vacuum. Separation and analysis of decomposition products showed that although secondary reactions between gaseous products and the solid phase had been greatly minimized, the measured decomposition was well advanced as evidenced by the detection of nitrogen in initial samples. The gaseous products are felt to be completely identified as N<sub>2</sub>, CO<sub>2</sub>, CO, N<sub>2</sub>O, NO, CF<sub>4</sub>, C<sub>2</sub>F<sub>8</sub>, COF<sub>2</sub>, NF<sub>3</sub>, HNF<sub>2</sub>, N<sub>2</sub>F<sub>2</sub>, N<sub>2</sub>F<sub>4</sub>, and HF.

(C) Extrapolation of decomposition rates from pressure-time data on poly FA-BDE to rates at zero time and the use of these rates in an Arrhenius plot produced an apparent activation energy for onset of decomposition of 44.4 kilocalories. This figure agrees well with the value 46 kilocalories obtained earlier from TGA data, and is consistent with the view that the initial decomposition step is the formation of difluoroamino free radicals.

(C) A further indication of the value of the activation energy required for onset of decomposition was given by a series of experiments run under continuous vacuum and the solid examined as a function of time and temperature. This work produced a value of 46.9 kilocalories.

(U) The thermal decomposition data obtained thus far on poly FA-BDE were found not to follow the kinetic equations for a first order reaction.

(C) The experiments on the slow thermal decomposition of INFO-635P were continued both in a vacuum and in the presence of the product gases. Present indications are that one of the initial steps is sublimation by proton transfer to the free amine and perchloric acid. Further decomposition then proceeds in the gas phase as well as in the solid. The decomposition is then further complicated by gas-solid reactions.

(U) An activation energy of 48 kcals. was derived from the pressure measurements. If the general mechanism proposed is correct, then the activation energy corresponds roughly to the gas phase decomposition.

(U) Attempts at identifying the residue are continuing and quantities of residue are being collected for further structural analysis.

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SECTION II

INTRODUCTION (U)

(U) The present report represents the progress made during the third quarter of a research program to obtain new, basic information on the kinetics and mechanism of decomposition of BTU, poly FA-BDE and INFO-635P. All three of these materials are solid, NF<sub>2</sub>-containing oxidizers with a high degree of spark and shock sensitivity. The present program has as its chief objective an understanding of the relationship between the decomposition mechanisms and the unusual sensitivity of these materials.

(U) The experimental approach being used has involved making slow thermal decompositions in monel systems at several temperatures in the classical manner. In addition, the technique of mass spectrometric analysis used in a new manner has been used throughout the work to gather information not easily obtainable by other means.

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SECTION III(U) DISCUSSION OF RESULTSA. THERMAL DECOMPOSITION OF INFO-635P (U)1. Decomposition in Presence of Product Gases (U)

(U) A series of experiments in the temperature range 150°-180°C. was made on powdered samples of INFO-635P. Each reaction was allowed to run for a twenty-four hour period. Because of the complexity of the decomposition mechanism<sup>1</sup>, the pressure curves did not comply with any of the equations developed from existing theories<sup>2</sup>. However, there is a more general method of analyzing the results from which activation energies can be derived. It is based on the assumption that a single kinetic equation is applicable over a specific small range of decomposition independent of the temperature. The rate equation is given the form:

$$F(\alpha) = kt \quad (1)$$

where k is the rate constant. The values of fractional decomposition are  $\alpha_n$ ,  $\alpha_{n+1}$ , at times  $t_n$ ,  $t_{n+1}$ .

(U) Then, over a finite range of decomposition:

$$F(\alpha_{n+1}) - F(\alpha_n) = k(t_{n+1} - t_n) \quad (2)$$

and at any different temperature, but the same values of  $\alpha$ :

$$F(\alpha_{n+1}) - F(\alpha_n) = k'(t'_{n+1}) = \text{constant} \quad (3)$$

From the Arrhenius equation it follows that a plot of  $\log(t'_{n+1} - t_n)$  against  $1/T$  is linear with slope  $E/2.303 R$ . Since the form of the kinetic equation  $F(\alpha)$  is not known, the pre-exponential factor cannot be found.

(U) The fractional decomposition ( $\alpha$ ) was assumed to be moles of gas produced per mole of INFO-635P originally loaded into the reactor. This is not a measure of the decomposition of the solid; however, based upon information developed from experiments in vacuo, Section III, A. 2,  $\alpha$  is believed to be more a measure of gas phase decomposition.

(U) Values of the activation energy for the decomposition of INFO-635P obtained by this method are given in Table I. The average value of  $E_a$  for the decomposition in the range of  $0.20 < \alpha < 0.5$  and  $0.5 < \alpha < 1.0$  are 48 and 35 kcal. respectively, in the temperature range 165°-180°C. The activation energy at 150°-160°C. in the range  $0.20 < \alpha < 1.0$  is 35 kcal. Since these activation energies are derived from pressure data, their interpretation mechanistically is difficult because of the complexity of the total decomposition. However, it is evident from the activation energies that there is a change in the decomposition mechanism.

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Table I

(U) Values of Activation Energy,  $E_a$ , for The Thermal Decomposition of INFO-635P in Different Temperature Ranges

| $\alpha$ range<br>mg./mL. | $E_a$ , kcal.<br>$150^\circ - 160^\circ\text{C.}$ | $E_a$ , kcal.<br>$165^\circ - 180^\circ\text{C.}$ |
|---------------------------|---|---|
| 0.10 - 0.15               | 58.6  | 26.9  |
| 0.15 - 0.20               | 88.8  | 42.1  |
| 0.20 - 0.25               | 38.6  | 45.3  |
| 0.25 - 0.30               | 27.6  | 50.9  |
| 0.30 - 0.35               | 36.3  | 50.0  |
| 0.35 - 0.40               | 32.4  | 45.3  |
| 0.40 - 0.45               | 35.5  | 47.6  |
| 0.45 - 0.50               | 37.9  | 50.0  |
| 0.50 - 0.55               | 28.0  | 40.6  |
| 0.55 - 0.60               | 28.5  | 32.1  |
| 0.60 - 0.65               | 32.4  | 44.9  |
| 0.65 - 0.70               | 34.2  | 34.6  |
| 0.70 - 0.75               | 31.3  | 35.5  |
| 0.75 - 0.80               | 38.8  | 33.5  |
| 0.80 - 0.85               | 37.7  | 43.5  |
| 0.85 - 0.90               | 39.4  | 29.1  |
| 0.90 - 0.95               | 35.5  | 35.6  |
| 0.95 - 1.00               | 34.3  | 36.8  |

The decrease in  $E_a$  with increasing pressure and constant temperature suggests either an autocatalytic reaction taking effect or that the predominant decomposition reaction has changed phase.

(C) Mass spectral analyses of the final gas products consistently show that the major products are  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$ , and  $\text{H}_2$ , as shown in Table II. No fluorine-containing compound in significant amount was observed, including  $\text{HF}$  gas. Minor products of methylamine, methyl chloride,  $\text{CF}_4$ ,  $\text{CNCl}$ , and 1,1- and 1,2-dichloroethane were also observed. The discrepancies in the mass balance relative to the product gases  $\text{N}_2$  and  $\text{HF}$  will have to be resolved by analytical techniques other than mass spectrometry.

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Table II(U) Mass Spectral Results from Total Decomposition of INFO-635P

| Temp.,<br>°C. | Mole Product/Mole INFO |                |                  |      |                | Total Moles<br>Gas/Mole INFO-635P |
|---------------|------------------------|----------------|------------------|------|----------------|-----------------------------------|
|               | CO <sub>2</sub>        | N <sub>2</sub> | N <sub>2</sub> O | CO   | H <sub>2</sub> |                                   |
| 160           | 2.49                   | 2.14           | 1.17             | 0.75 | --             | 7.21                              |
| 165           | 2.89                   | 2.23           | 0.85             | 0.77 | 0.11           | 6.969                             |
| 170           | 2.53                   | 1.88           | 0.94             | 0.89 | 0.10           | 5.22                              |
| 175           | 2.78                   | 2.08           | 0.83             | 0.84 | 0.16           | 6.869                             |
| 180           | 2.82                   | 1.93           | 0.86             | 0.96 | 0.14           | 6.901                             |

(C) The residues from these several reactions all had the same physical appearance and gave the impression that liquefaction had occurred. All samples were orange, and there seemed to be two different substances, one a solid and the other a tacky or amorphous substance. The residue was treated with acetone; the solid portion was insoluble and was set aside for further analysis. The tacky portion was soluble; it was re-precipitated as a pale yellow powder from acetone with ether. It is not sensitive; upon heating it begins to discolor at about 180°C. and finally decomposes with gas evolution. The resulting residue from this is similar in appearance to the acetone-insoluble material of the original sample. The tacky or amorphous form can be regenerated by dissolving the yellow powder in acetone and then allowing the solvent to evaporate. Infrared analysis of this soluble material suggests the presence of ClO<sub>4</sub><sup>-</sup>, C=O, or possibly fluorinated -C=C- and possibly a cyclic carbonate structure, Figure 1.

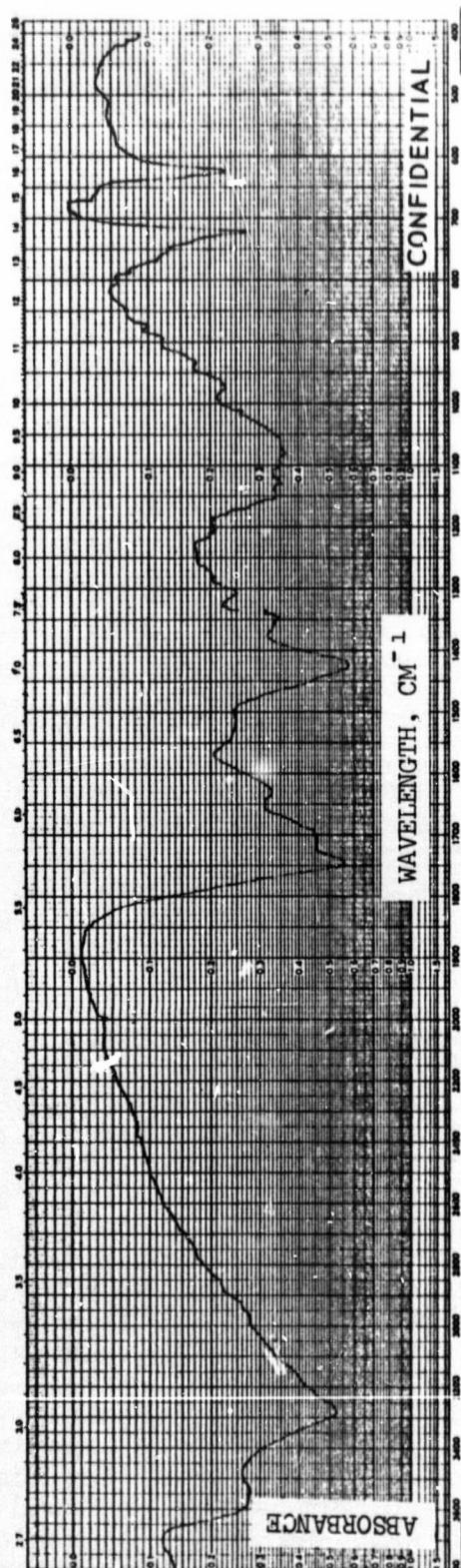
2. Vacuum Decomposition at 170°C. (U)

(C) The initial experimental results from the series of decompositions of INFO-635P run under vacuum conditions were given in the last quarterly report. Decompositions by this technique were continued to complete the series of 170°C. The percent weight loss curve appears to stabilize at about 85% Figure 2. The results are very regular. Mass spectral data of the product gases, Table III, show the general trend in the product gases as a function of time. Except for H<sub>2</sub>O, NO<sub>2</sub> and N<sub>2</sub>O which tend to disappear, all other products are steadily increasing. However, caution should be exercised in any quantitative interpretation of these results because of the reactivity of N<sub>2</sub>F<sub>4</sub> with water. Also the particular technique employed in performing these experiments does not allow the identification or determination of the non-condensable gases. Some of the minor gaseous products also found are C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>NH<sub>2</sub>, CNCI, C<sub>2</sub>H<sub>2</sub>F<sub>2</sub>, CF<sub>4</sub>, and SiF<sub>4</sub>. A liquid was also collected with these gases from the vacuum decompositions; however, once collected in the Kel-F trap the liquid could not be vacuum transferred out of the trap for analysis.

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(U) Fig. 1 - Infrared Spectra of Acetone Soluble Portion of Residue

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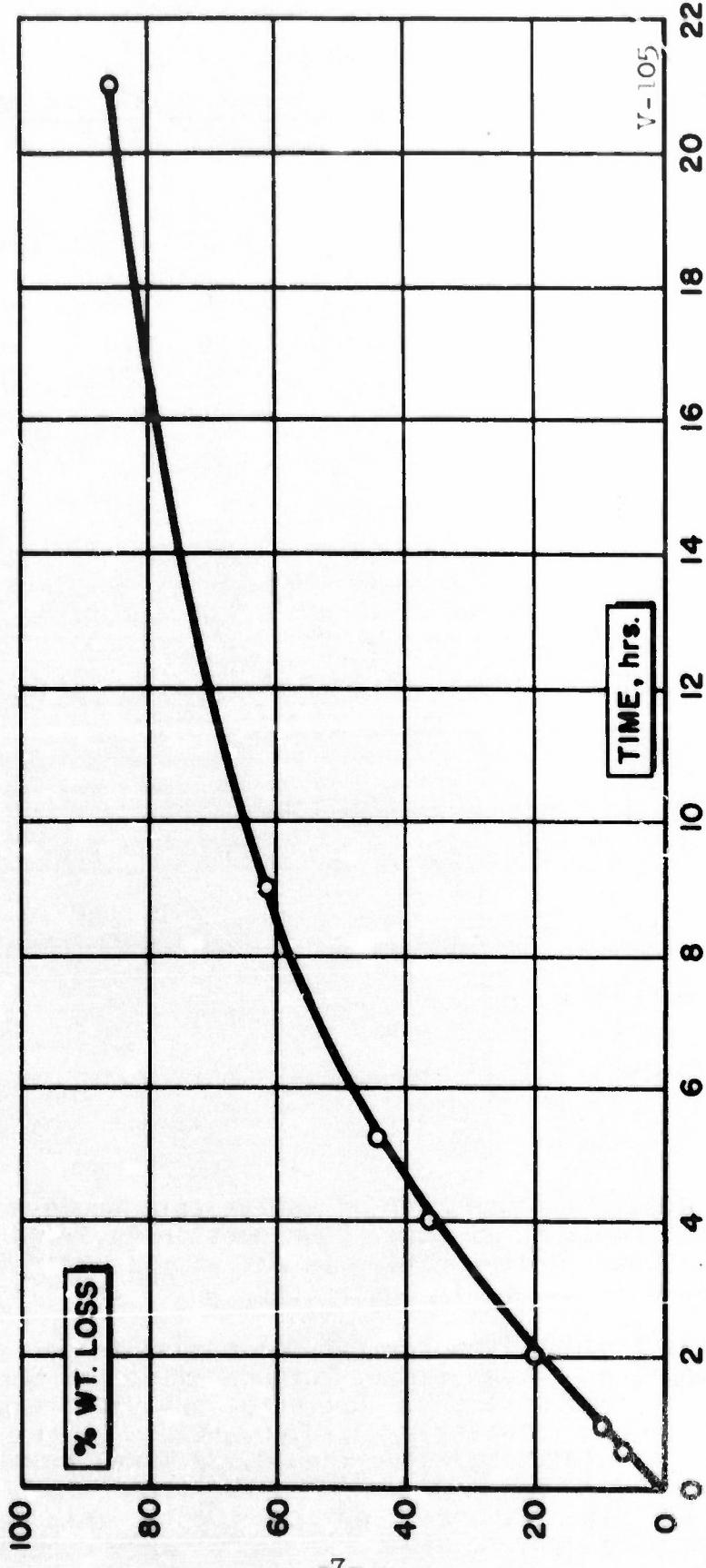


Fig. 2 - Percent Weight Loss of Solid INFO-635P at 170°C.

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**CONFIDENTIAL**Table III(U) Mass Spectral Results of Decomposition of INFO-635P at 170°C. in Vacuo

| Run No. | Time, hrs. | Resulting Compounds |                       |                                    |                      |                       |                                    | INFO-635P |
|---------|------------|---------------------|-----------------------|------------------------------------|----------------------|-----------------------|------------------------------------|-----------|
|         |            | Mole NO             | Mole N <sub>2</sub> O | Mole Major Product/NO <sub>2</sub> | Mole CO <sub>2</sub> | Mole H <sub>2</sub> O | Mole N <sub>2</sub> F <sub>2</sub> |           |
| 628     | 1          | 0.003               | 0.024                 | 0.003                              | 0.057                | 0.035                 | 0.003                              | 0.024     |
| 630     | 2          | 0.049               | 0.041                 | 0.009                              | 0.170                | 0.018                 | 0.031                              | 0.074     |
| 76      | 4          | 0.102               | 0.088                 | 0.020                              | 0.351                | 0.020                 | 0.068                              | 0.177     |
| 726     | 9          | 0.25                | 0.123                 | 0.017                              | 0.703                | --                    | 0.047                              | 0.276     |
| 728     | 21         | 0.271               | 0.081                 | --                                 | 0.991                | --                    | 0.106                              | 0.480     |

(C) The residue from each of these runs was still a powder, in contrast to the total pressure runs where the impression of flow was observed. The color change varied progressively from white to pale yellow to orange as the time of decomposition increased. The results from a total ClO<sub>4</sub> and NH<sub>3</sub> analysis on the residue were discussed in an earlier report<sup>1</sup>. Active fluorine analysis of these residues gave the results shown in Table IV.

Table IV(C) Active Fluorine Analysis of INFO-635P Plus Residues

| Run      | Time, hr. | Fluorine Equivalents/mole |
|----------|-----------|---------------------------|
| Standard | --        | 5.3                       |
| 78       | 0.5       | ~5.3                      |
| 630      | 2         | 3.7                       |
| 76       | 4         | 4.4                       |

(C) Normally, the number of equivalents would be expected to decrease as a function of time. The data in Table IV do not verify this expectation. This increase in activity is believed due to the formation of NO<sub>2</sub>- groups in the residue which can also oxidize I<sup>-</sup>.

(C) The residue from Run 728 decomposed in vacuum after twenty-one hours appeared homogeneous. This material had a melting point of 237°C. with decomposition. Elemental analysis resulted in the following empirical formula C<sub>24</sub>H<sub>43</sub>N<sub>15</sub>O<sub>3</sub>eFCle. Emission spectroscopy on this sample showed less than 0.17% total metal present.

(C) High resolution mass spectroscopy of this residue at temperatures varying from 130°C. to 230°C. gave essentially the

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same spectrum as shown in Table V. As indicated from the mass spectral results, the principal component is  $\text{HClO}_4$  and its related mass fragments.

Table V

(C) High Resolution Mass Spectrum of Residue from Run 728

| <u>M/e</u> | <u>Assignment</u>           |
|------------|-----------------------------|
| 102        | $\text{HCl}^{37}\text{O}_4$ |
| 100        | $\text{HClO}_4$             |
| 87         | --                          |
| 85         | $\text{Cl}^{37}\text{O}_3$  |
| 83         | $\text{ClO}_3$              |
| 69         | $\text{Cl}^{37}\text{O}_3$  |
| 67         | $\text{ClO}_2$              |
| 64         | --                          |
| 54         | $\text{HOCl}^{37}$          |
| 52         | $\text{HOCl}$               |
| 53         | $\text{Cl}^{37}\text{O}$    |
| 51         | $\text{ClO}$                |
| 44         | --                          |
| 43         | --                          |
| 38         | $\text{HCl}^{37}$           |
| 37         | $\text{Cl}^{37}$            |
| 36         | $\text{HCl}$                |
| 35         | $\text{Cl}$                 |

(C) Thin layer chromatography of residues from two runs, Number 628 at 170°C. for one hour, and 712 at 150°C. for 12 hours, both gave the same results. There was one major impurity and one trace component, exclusive of  $\text{NH}_4\text{ClO}_4$ . The major impurity is basic and treatment with nonhydrin indicator give a deep purple color which suggests that it is a primary amine or an ammonium salt, but not  $\text{NH}_4\text{ClO}_4$  which is not very sensitive to nonhydrin indicator.

(U) Seven small samples of INFO-635P were loaded into Teflon cups and placed in separate glass tubes. These were then attached to a system by which a vacuum could be maintained on each sample concurrently. All tubes were immersed simultaneously into a 170°C. oil bath. The level of the oil was kept below the ground glass joint of the tube. A single tube was removed from the bath at approximately one-hour intervals.

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(C) The percentage weight loss for each sample was determined. Each residue was analyzed for unreacted INFO-635P by NMR. The analytical result is based upon the relative intensity of the  $(\text{NF}_2)_3\text{C}$ -peak of the unknown compared to a standard.

(C) It was also observed that at long immersion times some material had condensed into the cool part of the glass tube. The weight of the sublimed material for the past three points was determined, and was identified by infrared spectroscopy as INFO-635P. The results from this experiment are given in Table VI.

Table VI

## (U) Vacuum Decomposition of INFO-635P

| Run No. | Time, hrs. | Original Wt., g. | Wt. of Residue, g. | Percent  |                         |                               |
|---------|------------|------------------|--------------------|----------|-------------------------|-------------------------------|
|         |            |                  |                    | Wt. Loss | INFO Recovered as Subl. | INFO in Residue NMR $\pm 5\%$ |
| 1       | 0.5        | 74.1             | 69.6               | 6.07     | --                      | 84.2                          |
| 2       | 1          | 86.6             | 78.6               | 9.27     | --                      | 99.1                          |
| 3       | 2          | 69.6             | 45.9               | 34.05    | --                      | 92.7                          |
| 4       | 3          | 79.3             | 44.9               | 43.4     | --                      | 79.8                          |
| 5       | 4          | 70.6             | 23.9               | 66.1     | 38.0                    | 75.8                          |
| 6       | 5          | 74.0             | 10.6               | 85.7     | 57.5                    | 68.6                          |
| 7       | 6          | 69.4             | 0.4                | 99.4     | 67.4                    | --                            |

(U) The data indicate that sublimation is an important step in the decomposition mechanism, and that most of the residue is still INFO-635P. The NMR results were confirmed by infrared analysis of the residue.

(U) The initial work on vacuum decomposition, Figure 2, indicated that the percentage weight loss of the residues were very regular. From the present experiments, Table VI, the amount of residue remaining other than INFO-635P is very small which indicates that gas-solid interaction is extensive when INFO-635P is sublimed into a hot rather than a cool zone.

(C) Decomposition may thus proceed in the gas phase, as the free amine, in the solid or condensed phase as the amine salt, and as an interaction between the different phases. The extent of each reaction independent of the other will have to be determined.

3. Mass Spectral Study of the Thermal Decomposition (U)

(U) A portable cycloidal mass spectrometer on loan from the Chemical Physics Laboratory of The Dow Chemical Company, was

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attached to the vacuum decomposition system such that small amounts of gas products could be sampled through a needle valve while maintaining the vacuum over the solid cryogenically and mechanically.

(U) The principal reason for performing these experiments was to obtain a qualitative picture of the decomposition with respect to the gas phase. No quantitative correlation among the several runs should be made since no standard cracking patterns of the various compounds on this instrument were taken; therefore, as the higher mass fragments begin to appear the distinction between those lighter fragments due to the thermal decomposition and those due to the cracking pattern of the higher masses becomes more difficult.

(U) Even a complete intra-correlation of the ion intensities between different spectra of the same run should not be attempted over the entire time range because of the change in the sensitivity factor as the optimum operating pressure of the instrument is exceeded.

(U) Six decompositions were run in the temperature range 150°C. to 185°C. A representative spectrum at the various temperatures at approximately the same time were taken.

(C) Analysis of these spectra with respect to mass numbers 20, 36, 47, 52, and 53 was made and the ion intensities were plotted as a function of time (Figures 3 and 4). The most significant point of the reaction at 150°C. is that mass 52 ( $\text{NF}_2$ ) and mass 53 ( $\text{HNF}_2$ ) appear to have reached a steady state (Figure 3). Mass 47, assigned to  $\text{N}_2\text{F}$  from  $\text{N}_2\text{F}_2$ , is steadily increasing. Hydrogen fluoride is by far the most abundant species. Mass numbers 28 and 44 are very abundant and follow similar curves. From high resolution mass spectral data at 120°, 150°, and 160°C., mass 28 and 44 are predominantly  $-\text{CH}_2\text{NH}_2$  and  $\text{CH}_2\text{CH}_2\text{NH}_2^+$ .

(C) Figure 4 represents similar curves of the data derived from the decomposition at 170°C. and agrees with the 150°C. run, Figure 3, except that  $\text{N}_2\text{F}_2$  ( $M/e = 47$ ) has also reached a steady state. Hydrogen fluoride is again the predominant species.

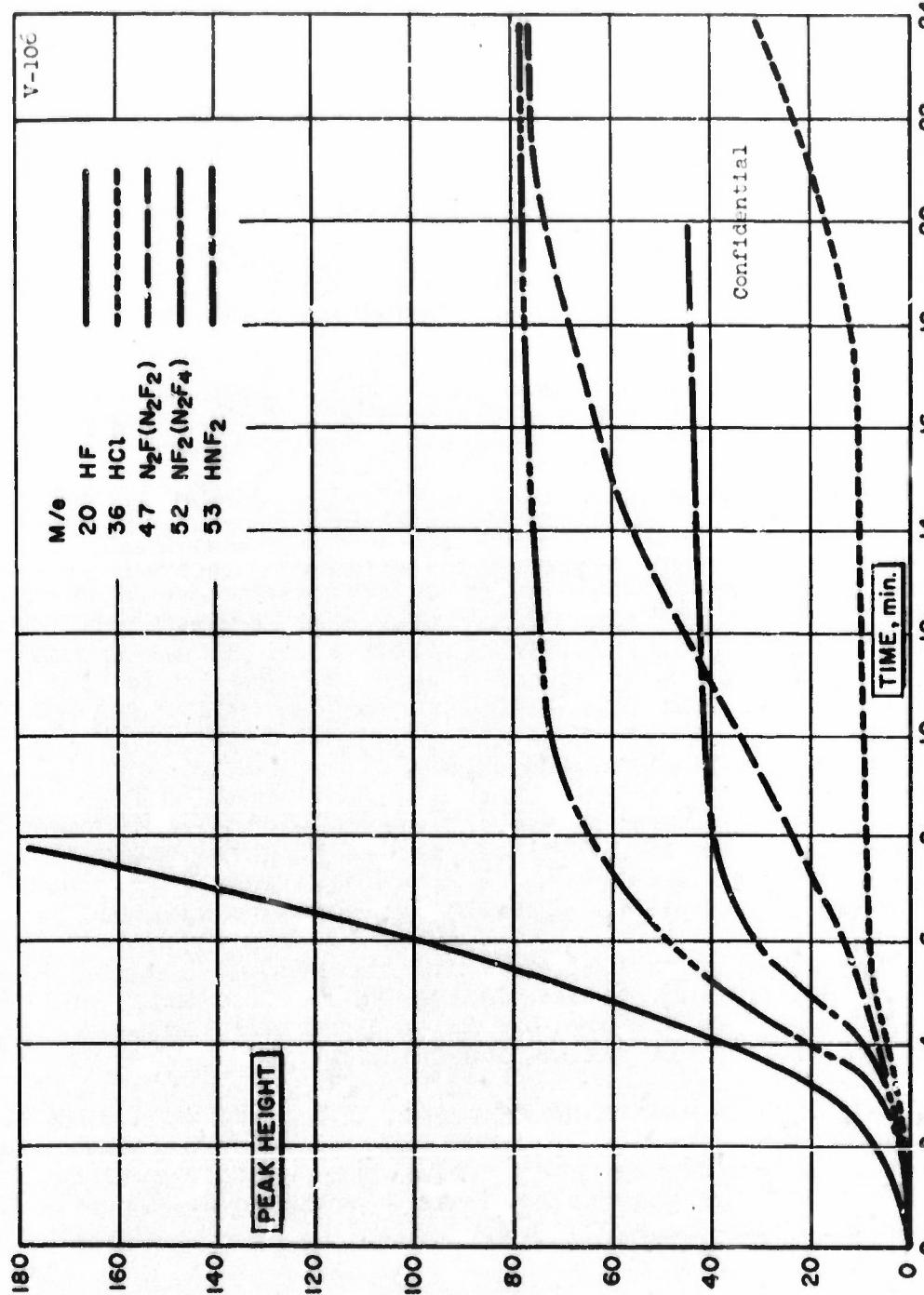
(C) The higher mass fragments are observed at longer times. Mass numbers 228 and 168, corresponding to the free amine and  $(\text{NF}_2)_2\text{C}_2$ , indicate that sublimation is an important factor in the decomposition under these vacuum conditions.

(C) The various oxides of chlorine,  $\text{ClO}_x$ , corresponding to the  $\text{HClO}_4$  cracking pattern, are also observed; however, their relative intensity is not very great during the reaction period, suggesting that the perchloric acid has reacted in some way either with the solid or the metal system.

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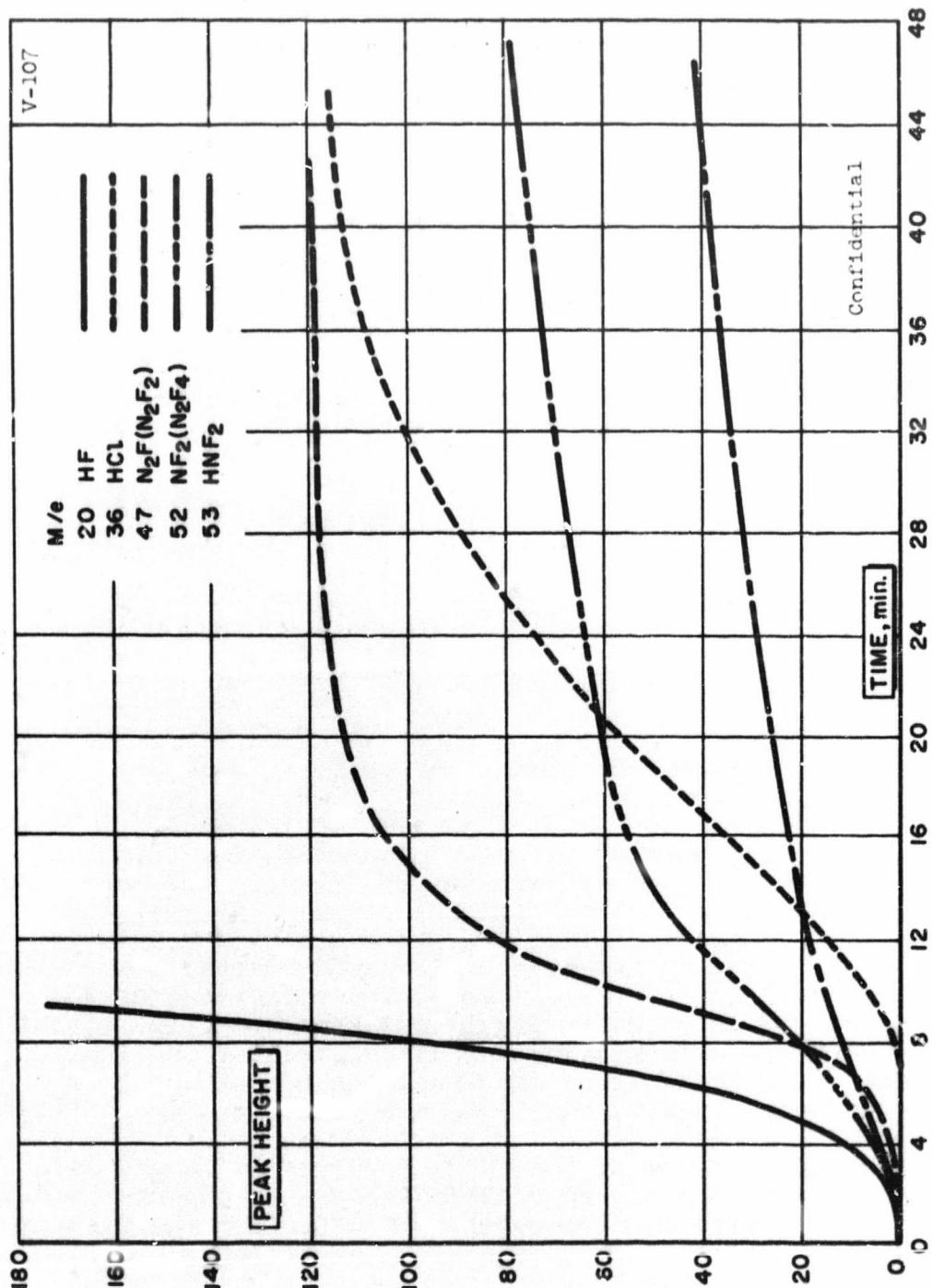


(U) FIG. 3 - Mass Spectral Peak Height as a Function of Time of Selected Gaseous Products from Vacuum Decomposition of INFO-635P at 150°C.

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(U) FIG. 4 - Mass Spectral Peak Height as a Function of Time of Selected Gaseous Products from Vacuum Decomposition of INFO-635P at 170°C.

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**CONFIDENTIAL****B. POLY FA-BDE (U)****1. Thermal Decompositions (U)**

(C) In the Second Quarterly Report a value of 46 kilocalories was reported for the apparent activation energy,  $E_a$ , for the initial decomposition step for poly FA-BDE. This value was obtained from thermogravimetric analyses (TGA) in which the weight loss of poly FA-BDE was recorded versus time at five different temperatures and under continuous evacuation. For the Arrhenius plot of log rate of weight loss versus  $1/T$ , the rate of weight loss used was taken as close to zero time as the data would permit. This was done to get a value of  $E_a$  which would represent the initial decomposition reactions.

(C) During the present period, values for  $E_a$  were obtained from different types of experiments and were found to agree reasonably well with the 46 kilocalories obtained from TGA.

(C) As mentioned in the last report, in order to minimize reactions of decomposition gases with the solid substrate (especially  $N_2F_2$ ,  $N_2F_4$  and  $HNF_2$ ), thermal decompositions were run in which the pressure of decomposition gases was not allowed to exceed 6 millimeters. The gases were then sampled and the monel decomposition vessel evacuated to zero pressure. The process was repeated several times during the initial and acceleratory phases of the decompositions. The pressure-time record took the form shown schematically in Figure 5. The data provided a record of the average rates of decomposition in terms of pressure at a series of average times. Knowing the monel reactor volume, the pressure, and the constant temperature used, the moles of gas were calculated and the rates of decomposition expressed in terms of millimoles of gas evolved. A series of average rates,  $r_1, r_2, \dots, r_n$  were thus obtained at corresponding average times  $t_1, t_2, \dots, t_n$  and, when plotted, the rate of gas evolution,  $r_0$ , at  $t=0$  was extrapolated. A value of  $r_0$  was obtained for each of the experimental temperatures. An Arrhenius plot of  $\log r_0$  values versus the reciprocal of the absolute temperature is shown in Figure 6. From the slope of this plot, a value of 44.4 kilocalories was calculated for the apparent activation energy of the initial decomposition reaction. This value compares favorably with that obtained from the TGA experiments.

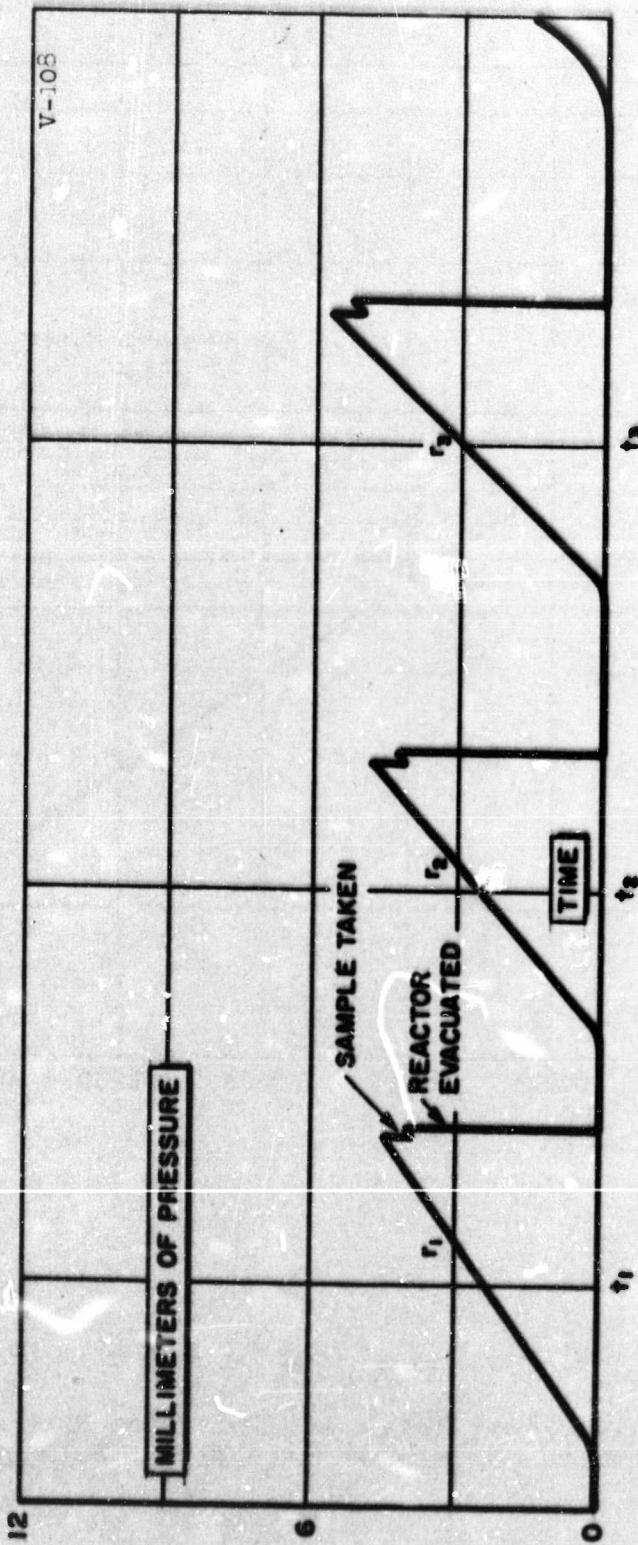
(C) During this course of the above experimental work, each sample taken was analyzed by vapor phase chromatography over a column packed with 30% siloxane on Chromosorb W at 0°C. For the last experiment in this series, a portable mass spectrometer was attached to the VPC exit tube to identify and to determine the order of elution of the various decomposition gases. The spectrometer was used on all five of the samples taken during the course of this experiment. Examination of the mass spectral data revealed that most of the VPC peaks were not "pure" as was assumed earlier. With the possible exception of  $HNF_2$ , the peaks were composed of at least two, and sometimes, three or four components. This made construction

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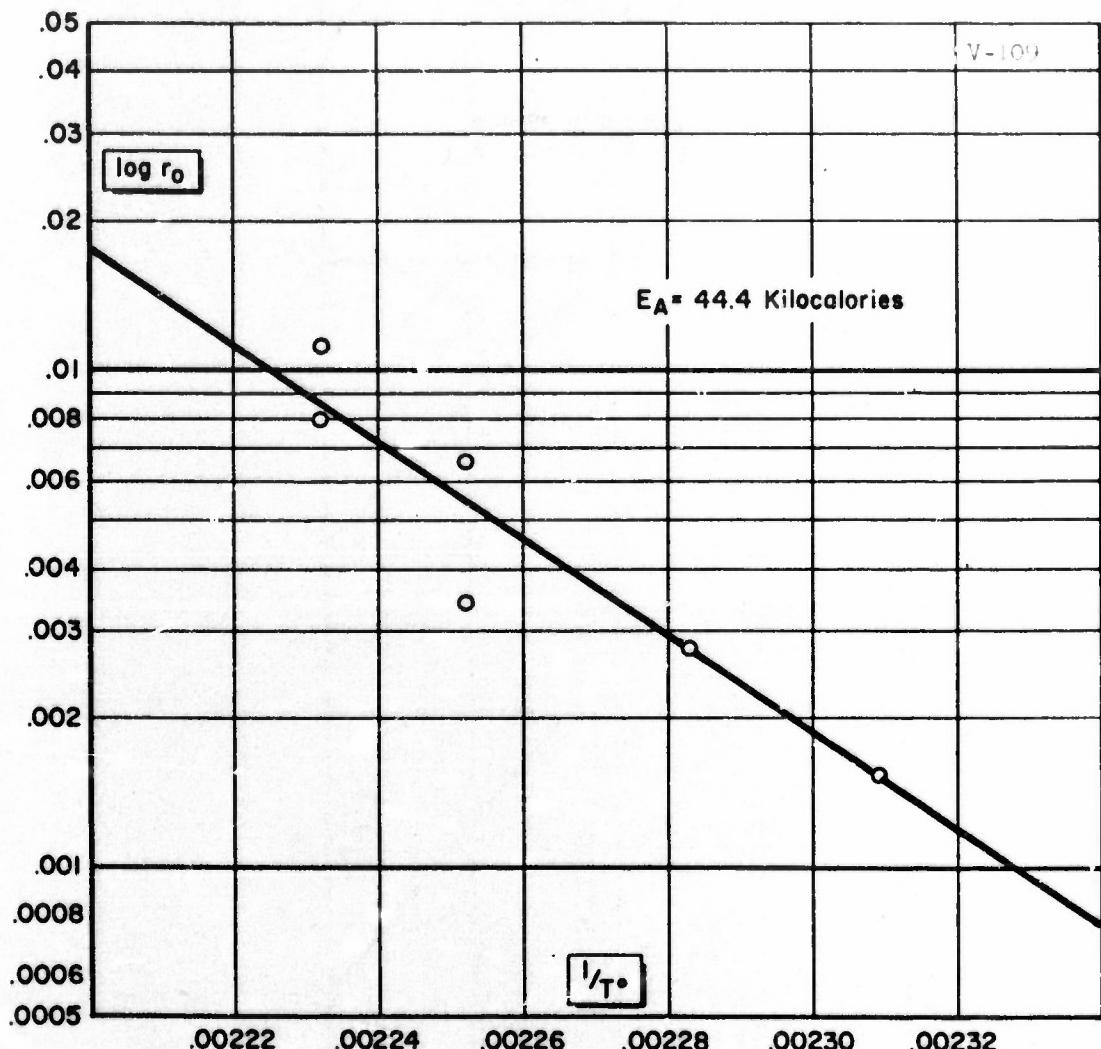
(U) Fig. 5 - Schematic of Pressure-Time Data on Poly FA-BDE

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(U) Fig. 6 - Arrhenius Plot; Total Gas Evolution Rate at Zero Time; Millimoles per Minute per 200 Mg. Poly FA-BDE

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of concentration plots of individual gaseous components impossible. This experiment also showed that  $N_2F_2$  is an early product.  $N_2F_2$  had not been previously identified. The mass spectral analyses confirmed the production of the gases listed previously as being produced during the decomposition of poly FA-BDE, viz.,  $N_2$ , NO,  $N_2O$ ,  $CO_2$ , CO,  $N_2F_4$ ,  $HNF_2$ ,  $COF_2$ ,  $NF_3$ ,  $CF_4$ ,  $C_2F_8$ , and HF. Of these products, NO and  $N_2O$  contributes the least to the total gas pressure above decomposing poly FA-BDE. That portion of gas samples taken for VPC analysis which was non-condensable in a liquid nitrogen trap was the most abundant fraction as judged by its relative peak height. These non-condensable portions consisted of nitrogen and undetermined amounts of CO. Assuming peak heights as an approximate quantitative measure, this fraction represented about half the total gas pressure throughout most of the thermal decomposition studied. If the average rate of non-condensable gas formation is calculated from the experimental data and use made of the peak heights obtained in the VPC analyses, a rate of  $N_2+CO$  formation at zero time can be extrapolated for each temperature. This was done for four temperatures for which the data were complete. The values of  $r_0$  so obtained are shown on an Arrhenius plot in Figure 7. Considering the assumption necessary to make this plot, the apparent activation energy of 49.4 kilocalories calculated in this way is in reasonable agreement with that found by using the rates of total gas evolution.

(U) Attempts were made to fit the pressure-time data obtained in the earlier studies of poly FA-BDE decomposition to theoretical equations reported in Garner's "Chemistry of the Solid State." These attempts have been unsuccessful. The decomposition of poly FA-BDE is a very complex one and the methods used in this work, in the main, have recorded information on a decomposition already well advanced when the first samples were taken for analysis. That this is true is evidenced by the large amounts of nitrogen found in these first samples, indicating that a substantial amount of reaction had already taken place in the polymeric network. Only in MTA and high resolution mass spectrometry was the main early decomposition product found not to be nitrogen but  $NF_2$  radicals. Thus, the reactions leading to nitrogen formation were held to a minimum because of the very high vacuum of the mass spectrometer and the use of milligram size samples.

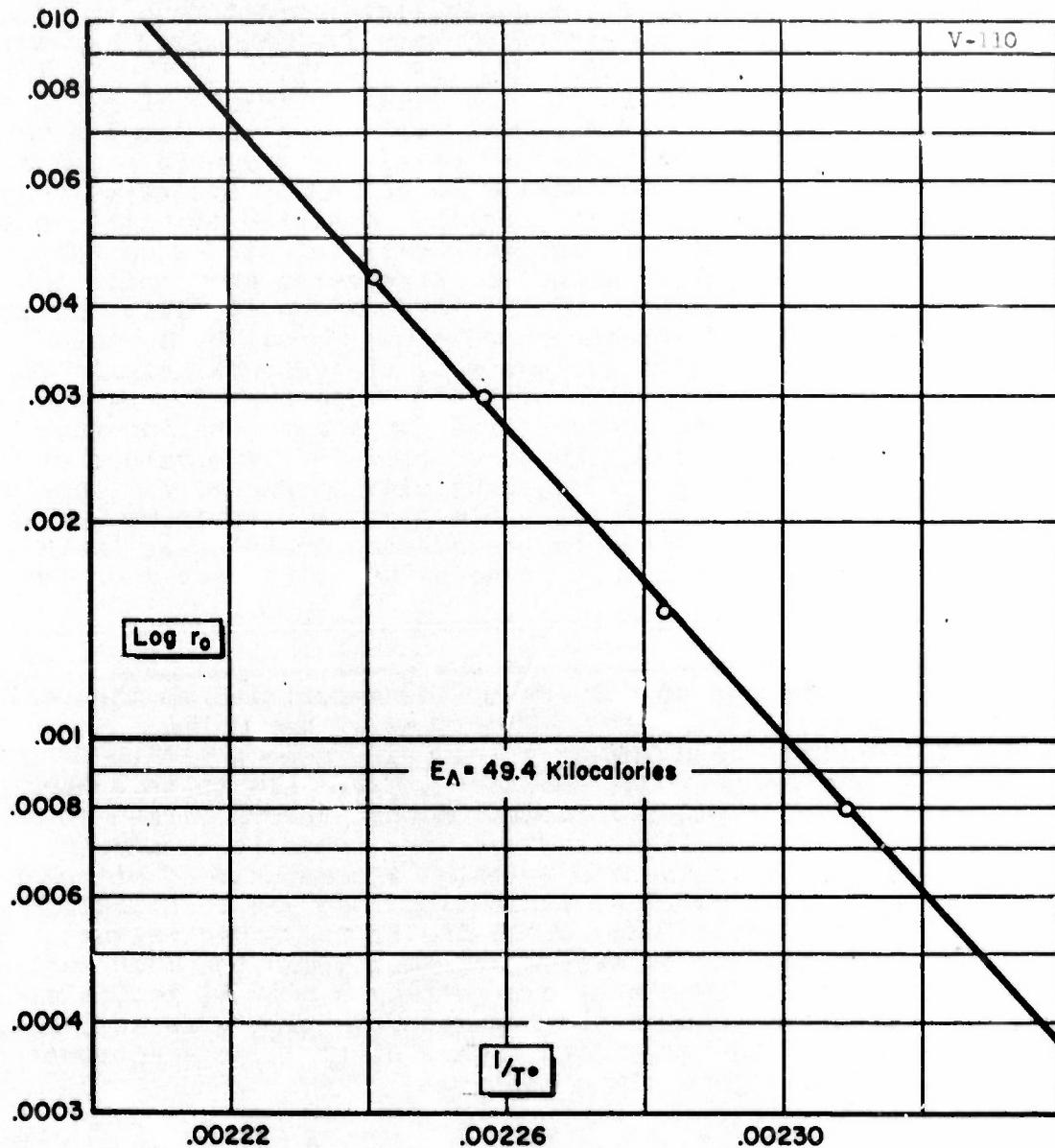
(C) Near the close of the last quarter, a method was found whereby it appeared to be possible to approximate the disappearance of poly FA-BDE. In this method, samples of the polymer are decomposed under continuous vacuum for various periods of time and the solid residues treated with Freon 113. The Freon-soluble portion was found to give an infrared spectrum identical to the original polymer, was near white, and very shock sensitive. Elemental and active fluorine analyses of this fraction are shown in Table VII. The insoluble portion was found to be slightly shock sensitive, amber, and had an infrared spectrum which indicated that some absorption in the  $NF_2$  region remained. Elemental and active fluorine analyses are also shown in Table VII. These data provide

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(U) Fig. 7 - Arrhenius Plot;  $N_2(+CO)$  Rate at Zero Time;  
Millimoles Gas per Minute per 200 Mg. Poly FA-BDE

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some justification for the assumption that the Freon-soluble fraction represents a statistical proportionality to the amount of poly FA-BDE yet undecomposed. On this basis, experiments were carried out at four different temperatures. At each temperature, samples of partially decomposed poly FA-BDE were removed at intervals from the constant temperature bath and the Freon-soluble portion separated. The results of these experiments are plotted in Figure 8 as percent of original sample weight that was Freon-soluble at the indicated time intervals. As in the case of the pressure-time data mentioned earlier, these data did not follow a first order plot and initial attempts to fit the data to an equation failed. Initial decomposition rates were applied to an Arrhenius plot to obtain a value for  $E_a$ . The result, 46.9 kilocalories, shown in Figure 9, is in fair agreement with the values obtained by the methods described earlier.

Table VII

(U) Analytical Data on Freon 113-Soluble and Insoluble Fractions from Poly FA-BDE Decomposition

| <u>Element</u>      | <u>Percentage Composition</u>   |                                   |                                     |
|---------------------|---------------------------------|-----------------------------------|-------------------------------------|
|                     | <u>Original<br/>Poly FA-BDE</u> | <u>Freon-Soluble<br/>Fraction</u> | <u>Freon-Insoluble<br/>Fraction</u> |
| Carbon              | 16.4 calc.                      | 16.8                              | 20.5                                |
| Hydrogen            | 1.35 calc.                      | 1.4                               | 1.72                                |
| Nitrogen            | 19.2 calc.                      | 20.4                              | 16.4                                |
| Fluorine<br>(total) | 52.1 calc.                      | 50.9                              | 43.9                                |
| Active<br>fluorine* | 38.0                            | 36.1                              | 25.8                                |
| Molecular<br>weight |                                 |                                   | --                                  |

\* By titration of iodine liberated from sodium iodide in acetone solution.

C. BTU (U)

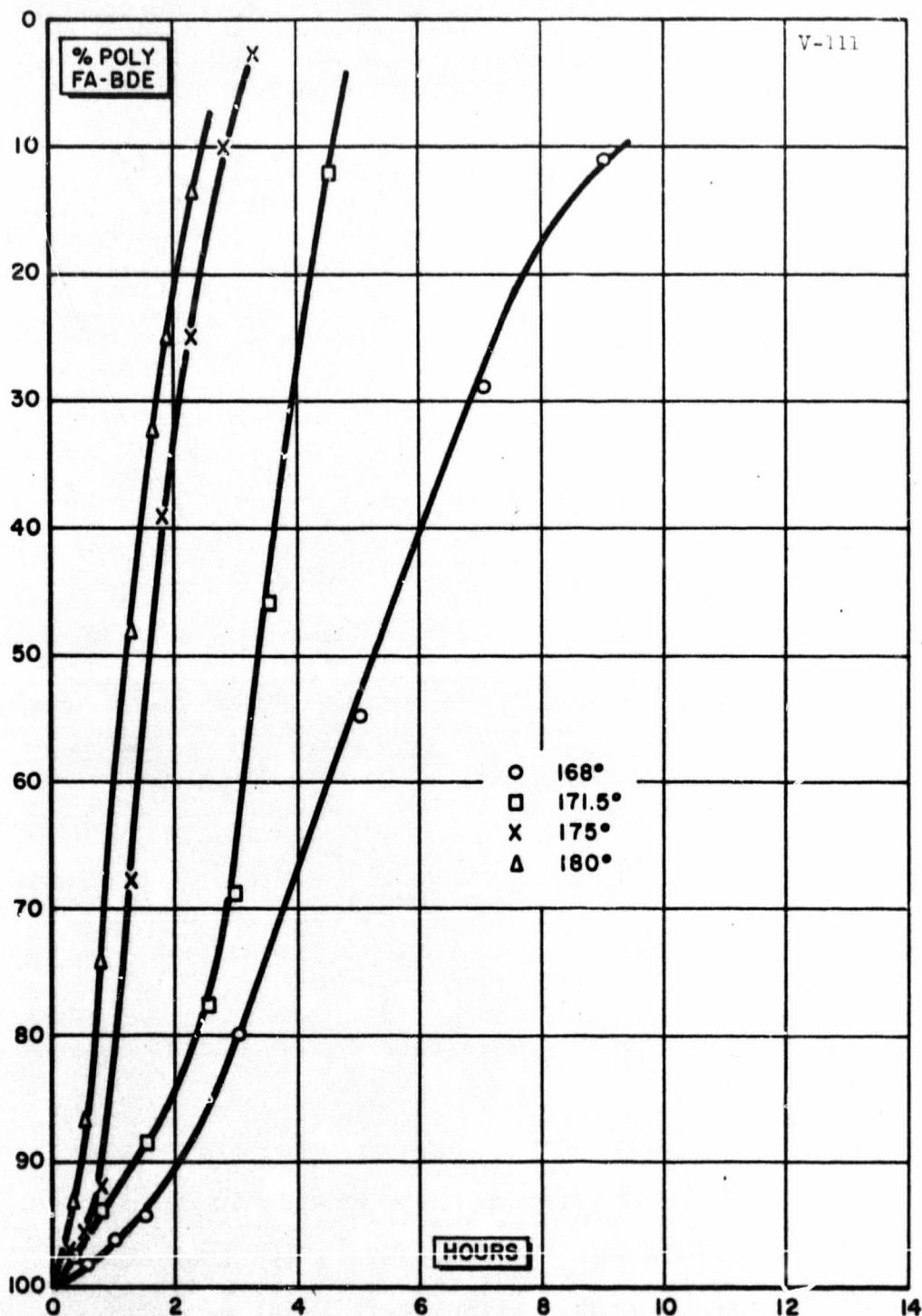
(C) Two preliminary experiments were made in which approximately 100 milgram samples of BTU were thermally decomposed in the monel system. In one experiment the temperature was increased slowly from room temperature to 185°C.; in the other, a decomposition was made at 130°C. Both decompositions left a yellow solid residue, and infrared analysis of the final product gases indicated the presence of CO<sub>2</sub>, NF<sub>3</sub>, CF<sub>4</sub>, HF, and TRIS-I. The pressure-time data implied that sublimation of BTU might be the first step followed by decomposition in the gas phase.

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(U) Fig. 8 - Disappearance of Poly FA-BDE as Measured by Freon 113 Solubility

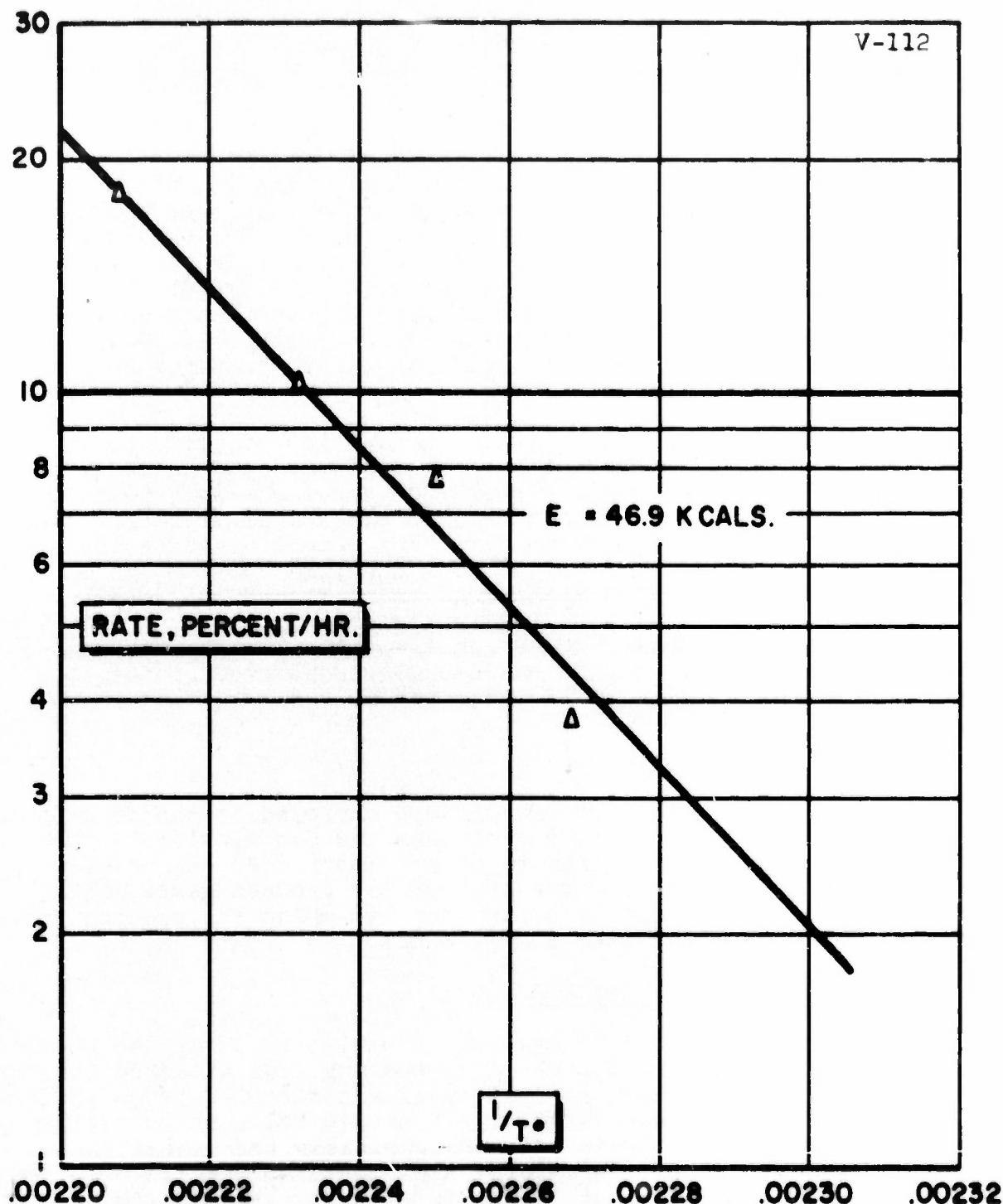
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(U) Fig. 9 - Arrhenius Plot; Rate of Disappearance  
of Poly FA-BDE

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**CONFIDENTIAL**SECTION IVEXPERIMENTAL (U)A. THERMAL DECOMPOSITION (U)1. Poly FA-BDE (U)

(C) The apparatus and technique of performing the slow thermal decompositions and subsequent separation and analysis of decomposition products were described in earlier reports. During the present period, the experiments on poly FA-BDE were done with the pressure of the decomposition gases regulated at a few millimeters to minimize reaction of evolved  $N_2F_2$ ,  $N_2F_4$  and  $HNF_2$  with the solid substrate. This was accomplished by allowing the pressure to build up to the desired level and then expanding and condensing the gases in the sampling unit of the system.

(U) For the work in which the decomposition of solid poly FA-BDE was followed, weighed samples were placed into Teflon cups contained by individual glass vessels and continuously evacuated during the experiment. The samples were removed at different time intervals and treated with Freon 113. The weight of the soluble portion, which gave an infrared pattern identical to the original poly FA-BDE, was taken as a measure of undecomposed poly FA-BDE. The insoluble portion was amber, slightly shock sensitive, and gave an infrared pattern similar to, but not identical with, undecomposed poly FA-BDE. A set of samples was decomposed at each of the four temperatures, 180°, 175°, 171.5°, and 168°C.

2. INFO-635P (U)

(U) Two experimental procedures were employed in the decomposition studies of INFO-635P. The technique and description of the apparatus were given in earlier reports. The procedures briefly are: (1) decomposition in the presence of the product gases until completion, and (2) vacuum decomposition, in which the product gases were pumped off and collected continuously.

B. MASS SPECTROMETRIC TECHNIQUES (U)

(U) A portable cycloidal mass spectrometer, built at the Chemical Physics Laboratory of The Dow Chemical Company, was attached to the vacuum decomposition system so that small amounts of gaseous products could be sampled continuously through a needle valve while maintaining the vacuum over the solid both cryogenically and mechanically. The instrument was also used by attaching the sampling line of the spectrometer to the exit tube of the VPC unit for the experiment on poly FA-BDE. The mass spectra were recorded with a Visicorder.

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SECTION VCONCLUSIONS AND FUTURE WORK (U)A. INFO-635P (U)

(U) The reactions under pressure of gaseous products have indicated that the decomposition involves gas-gas and gas-solid interactions as well as solid decomposition. In addition, there is some evidence of melting or of a solution being formed or that the reaction proceeds by an autocatalytic mechanism, which would account for the sigmoid pressure-time curve.

(C) Vacuum decompositions of INFO indicate that CO<sub>2</sub>, N<sub>2</sub>F<sub>4</sub>, NO, N<sub>2</sub>F<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> are major products of decomposition with CO<sub>2</sub> being predominant; HF is most likely a product, too, but it is not observed. A quantitative determination of HF as a final product will be attempted. Vacuum techniques have decreased the amount of solid decomposition over a given time period as evidenced by the weight loss.

(C) Mass spectrometric analysis of the decomposition gases as they are produced strongly indicates that sublimation is one of the initial steps. The large mass fragments observed, 228, 207, 168, support this conclusion. The continuous mass spectrometric analysis of the product gases from the vacuum decomposition shows that HF is a large and increasing fraction of the gases. Since HF is an expected product of the mass cracking pattern of the large fragments in the mass spectrometer as well as from the decomposition of solid INFO and of the free amine of INFO, no definite conclusion can be made as to its primary source.

(C) An attempt will be made to obtain the cracking pattern of the free amine in the portable cyclodial mass spectrometer which will allow the derivation from the existing spectra data most closely related to the deomposition.

(U) A review of the early MTA work in the light of present knowledge suggests that the double reaction sequences observed are associated with the sublimation and eventual decomposition of the residual material.

(C) The mechanism implied by all these data is the sublimation of INFO-635P by dissociation:



as the first step, with the subsequent decomposition of the free amine in the gas phase.

(C) An attempt wil be made at separating the gas phase decomposition from the gas-solid reaction. This will allow a qualitative interpretation of relative amount of interaction, and of the rate of gas phase decomposition of the free amine.

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(U) An apparatus will be designed to allow the rate of solid decomposition and the resulting gaseous products to be determined free from the complicating sublimation and gas phase decompositions.

(C) The hydrogen chloride salt of INFO will be made by reacting the acetone solutions of the perchlorate salt with tetramethylammonium chloride. The resulting tetramethylammonium perchlorate is insoluble, leaving the chloride salt of INFO in solution. Several decompositons will be run to determine the effect of  $\text{ClO}_4^-$  ion on the decomposition.

(U) As decompositions are made, soluble and insoluble residue samples will be separated and collected. Identification will be attempted when a sufficient quantity of material has been accumulated.

B. POLY FA-BDE (U)

(C) The experimental data obtained this period again indicate the complex reaction sequence that must prevail when poly FA-BDE is decomposed. Values for the activation energy for onset of thermal decomposition were calculated from experimental data as 44 to 49 kilocalories, depending on the method used. These values are consistent with the view of a free radical mechanism, initiated by the cleavage of the C-N bond to form  $\text{NF}_2$  free radicals. That this does indeed occur was shown in the work reported earlier using MTA and high resolution mass spectrometry on milligram size samples under high vacuum. These experiments indicated that no large volatile fragments were produced in the initial decomposition stage and the mass spectra were overwhelmed by masses 52 ( $\text{NF}_2$ ) and 33 (NF) at  $135^\circ\text{-}140^\circ\text{C}$ . Although nitrogen was observed immediately in the decomposition, it represented only a minor part of the spectra. However, it soon became one of the largest peaks in the spectra after decomposition started. In the slow thermal decomposition work, the formation of nitrogen was immediate and substantial and remained the major contributor to the measured gas pressure. Since the formation of large amounts of nitrogen still occurred when the decompositions were performed under low pressure to minimize gas-solid reactions, one must conclude that substantial reaction occurs in the matrix of the solid polymer. Thus, the activation energies calculated from pressure-time curves were obtained from data on a complex reaction sequence and may only represent an approximation to the  $E_a$  necessary for onset of decomposition. This objection does not apply to the  $E_a$  obtained from the experiments in which Freon-soluble material was plotted as a function of time. Thus, the value 46.9 kilocalories is the more meaningful if the basic assumption made in these experiments is valid.

(U) Future work on poly FA-BDE will consist chiefly of trying to postulate mechanistic paths that will give reasonable explanations for the experimental facts. It is felt that the initial step of the decomposition has been identified and final products characterized. In addition, most of the gaseous intermediates have been identified. Rates for the onset of decomposition have been measured for the

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disappearance of poly FA-BDE and for gas production, and from these data activation energies have been calculated. A more accurate mass balance of the experimental data is still required. Both of these topics will be emphasized in the future work on poly FA-BDE.

## C. BTU (U)

(U) The thermal decomposition studies already begun on BTU will represent the major experimental effort in the last quarter of this year. Although initial experiments indicate that the decomposition of this material proceeds from the gas phase following sublimation as a first step, this should be confirmed before more extensive experimentation is done. Once the general character of the initial decomposition has been affirmed, the necessary experiments to obtain the needed kinetic information can be planned and executed.

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## XVI. ABSTRACT

The purpose of this research has been to study the thermal decomposition of the solid oxidizers, INFO-635P, poly FA-BDE, and BTU, to obtain knowledge of their decomposition kinetics and mechanism.

Thermal decompositions of poly FA-BDE were continued with additional experiments in the temperature range 160° - 180°C. The work was done both at low pressure of decomposition gases and under continuous vacuum. Separation and analysis of decomposition products showed that, although secondary reactions between gaseous products and the solid phase had been greatly minimized, the measured decomposition was well advanced as evidenced by the detection of nitrogen in initial samples. Extrapolation of decomposition rates from pressure-time data on poly FA-BDE to rates at zero time and the use of these rates in an Arrhenius plot produced an apparent activation energy for onset of decomposition of 44.4 kcal. A series of experiments in which the solid polymer was examined as a function of time and temperature as it decomposed under continuous vacuum produced a value of 46.9 kcal.

The experiments on the slow thermal decomposition of INFO-635P were continued both in a vacuum and in the presence of the product gases. Present indications are that one of the initial steps is sublimation by proton transfer. Further decomposition then proceeds in the gas phase as well as in the solid. The decomposition is then further complicated by fast-acid reactions. If the general mechanism proposed is correct, then the activation energy of 48 kcal. derived from the pressure measurements corresponds roughly to the gas phase decomposition.

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|---|--|--------|----|--------|----|--------|----|
|   |  | ROLE   | WT | ROLE   | WT | ROLE   | WT |
|   | INFO-635P  |        |    |        |    |        |    |
|   | INFO-635P, Decomposition of  |        |    |        |    |        |    |
|   | FA-BDE, Poly   |        |    |        |    |        |    |
|   | FA-BDE, Poly, Decomposition of   |        |    |        |    |        |    |
|   | BTU  |        |    |        |    |        |    |
|   | Thermal Decomposition of Oxidizers   |        |    |        |    |        |    |
|   | Decomposition  |        |    |        |    |        |    |
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